research review

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New Superconductors Discovered

MAX SWERDLOW, Directorate of Physical Sciences, AFOSR

A new category of superconducting materials has been discovered by scientists at the University of California, San Diego, under the direction of Professor Bernd T. Matthias. This was achieved in collaboration with scientists at the California Institute of Technology under the direction of Professor Pol Duwez. Both professors are AFOSR principal investigators. These scientists have demonstrated, through a series of experiments, that it is possible to synthesize new superconducting substances from elements which do not combine under normal conditions of crystal growth. These results were published recently in Science[1], and as a doctoral thesis[2].

The superconducting alloys found by the scientists are metastable compounds--compounds which do not form and are not stable under normal conditions. The particular compounds prepared and investigated were synthesized from gold or silver, in combination with tellurium or germanium. None of these four is superconducting as a pure element. In fact, the last two are not even metals.

The metastable compounds were prepared using an ultrafast cooling technique developed by Professor Pol Duwez of Cal Tech[3] under AEC sponsorship. In this technique, sometimes called "splat cooling," a droplet of liquid alloy is blasted against a copper surface by a jet of gas. The liquid metal spreads out into a thin foil and cools very rapidly by conduction to the copper. The alloy has been estimated to cool at the incredible rate of more than 4,000,000 degrees Fahrenheit a second.

When the alloy is quick-frozen in this manner, the atoms do not have time to align themselves into normal patterns. Instead, a new pattern is formed with new chemical and electrical properties. An example is an alloy of four parts of silver to one of germanium. If melted and mixed together in the liquid state and allowed to cool in a normal manner, the solid will consist of a mixture of grains of germanium interspersed with grains of silver. Neither of these is superconducting nor is the mixture.

The scientists found, however, that when the liquid was quick-frozen by the "splat-cooling" technique, the atoms of silver and germanium arranged themselves in a regular array and the solid was homogeneous rather than a mixture of two different materials. Furthermore, the new silver-germanium compound was found to become superconducting at a sufficiently low temperature.

The ability of superconducting wire to

carry an electric current without loss is the basis of an important industrial application: superconducting magnets. Superconductivity, a phenomenon found in many, but not all metals at temperatures near absolute zero (zero degrees on the Kelvin scale or -459.72 degrees Fahrenheit) is the complete disappearance of electrical resistance resulting from a "condensation" of the conduction electrons into a state of frictionless motion.

The nature of the superconducting state is still a subject of active research. Different metals and alloys vary considerably in their superconducting properties. For instance, the transition temperatures (the highest temperature at which a particular metal will superconduct) vary from near absolute zero to a high of 18 degrees Kelvin (-427.32 degrees Fahrenheit). A compound of niobium and tin (Nb_3Sn) at 18 degrees Kelvin has the highest transition temperature now known. Lead, tin and zinc, three common metals, are superconducting at 7.2, 3.7 and 0.9 degrees Kelvin, respectively. Copper, silver and gold, on the other hand, show no superconductivity down to the lowest temperatures at which they have been tested (about 0.020 degrees Kelvin). The new superconductors found in the current study are important in that they point to the possibility of making superconductors with special desired properties, such as transition temperatures above 18 degrees Kelvin, without being restricted by the normal rules of chemistry.

Despite the fact that neither silver nor germanium by themselves are superconducting, the silver-germanium compound was found to become superconducting with a transition temperature of 0.85 degrees Kelvin. Similarly, a new compound of silver and tellurium ($AgTe_3$) was prepared and found to be superconducting at 2.6 degrees Kelvin. Other new gold-germanium and gold-

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JACOB SEIDEN
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tellurium compounds were found to become superconducting at various temperatures between 1.0 and 1.6 degrees Kelvin.[2]

The very-low temperatures required for these studies were achieved with the aid of liquid helium. Ordinary liquid helium-4 (He^4) was used for temperatures down to about 1.1 degrees Kelvin. Lower temperatures, down to 0.3 degrees Kelvin, required a special apparatus utilizing the rare isotope helium-3 (He^3), which has only one neutron in its nucleus. (Ordinary helium has two neutrons in its nucleus.) The experimental alloy was immersed in the boiling liquid helium to bring it to superconducting temperatures. (The temperature of boiling He^4 is 4.2 degrees Kelvin at atmospheric pressure. The temperature can be lowered still further by reducing the pressure over it with a vacuum pump, just as water boils at lower temperatures at higher elevations.)

The question of the universality of the superconductivity phenomenon in metals has been a matter of considerable scientific interest and controversy in recent years. The phenomenon was originally thought to be a rare and uncommon occurrence in metals, requiring just the right combination of factors such as crystal structure, electronic radii, etc. As more and more superconductors have been discovered (the total number of superconducting compounds is now of the order of 1000), this view has gradually given way to the converse one, namely, that most, possibly all metals will superconduct if the temperature is low enough.

Superconductivity has previously been observed in pure iridium and in platinum-rich solid solutions, and it has previously been suggested that pure platinum may be superconducting at sufficiently low temperatures.[4] In a new paper,[5] the superconductivity of some intermetallic compounds has been reported. Eight of these compounds contain appreciable amounts of gold. This information is of interest because it tends to confirm the conjecture[6] that pure gold may eventually be found to be a superconductor at a sufficiently low temperature. The basis of this conjecture is that, if many gold-rich intermetallic compounds are found to be superconducting, then pure gold is likely to be a superconductor also. Although this may be a naive point of view, it seems to have a certain validity for other elements. The inference is made that superconductivity in the noble elements may extend from iridium through platinum, even as far as gold. With the eight new gold-rich superconductors reported, the conjecture that pure gold might be superconducting begins to sound less fanciful.

The possibility that pure gold might be a superconductor has, in turn, a bearing on another problem. It has been speculated[7] that even for "simple" metals like silver and sodium, some sort of phase change will occur in the electron gas at sufficiently low temperatures, causing the specific heat to go to zero faster than linearly. The question of whether or not pure gold is superconducting is important because it will help to decide whether this speculation is correct. At the present time, however, this is still a matter of belief; it has not at all been established that the electronic gas will condense to a superconducting state in every metal, or even in every diamagnetic metal. The problem cannot yet be discussed theoretically in a completely reliable way, and consequently all new experimental data on previously untested classes of compounds, crystal structures, atomic arrangements, etc. is relevant. ★

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HUMAN PERFORMANCE & THE PHYSICAL ENVIRONMENT

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The effects of environmental factors upon the performance of complex tasks is of particular importance in view of military and space requirements relating to the ability of man to perform under unusual conditions. Past studies in the area have confounded the easy expectations that such performance would benefit from so-called "optimum"conditions--quiet, free of the effects of sleep loss, etc. Studies concerned with the effects of temperature variations, noise, and the like, have produced paradoxical results; some have shown no resultant change in performance, some losses, and some improvements. By inference, the problem of achieving engineering control of the environment is made more complex by the consideration of both physiological and psychological reactions induced by operating stresses.

An attempt to systematize understanding of the factors involved is being made under an AFOSR grant by Dr. Warren H. Teichner, Professor of Psychology and Director of the Institute of Environmental Psychophysiology, at the University of Massachusetts. His approach emphasizes the importance of the psychophysiological interaction and attempts to define its components in studies of the effects of temperature, noise, and sleep loss, both singly and in combination.

One such study[1] by Dr. Teichner and his associates concerned the effects on a complex search task of continuous versus intermittent presentations of loud "white" noise. The study assumed that task performance is related to the level of arousal, and that this in turn would vary with the energy-time characteristics of the sound and with the ear's adaptive response. It was predicted from a model incorporating these assumptions that search time would be less the more continuous the sound early in the task, but that the reverse would obtain later. The results of the study supported this prediction and afforded collateral evidence for other aspects of the model.

At the same time, Dr. Teichner and his associates have been studying the applicability of the same kind of approach to performance under different thermal conditions. These experiments have required subjects to carry out tasks of prolonged attention in different temperatures while various measures of thermal bodily reactions were obtained. One recently completed study[2] along this line suggests that the concept of universally acceptable temperature conditions may be misleading--that rather, for some individuals, a warm environment is optimum--for others, a cool environment may be optimum--and for still others, the usual 72-80 degrees F. may be an optimum range. This study, along with others recently completed, suggests that the basis of these differences may lie in basic individual differences in body-temperature regulation.

These same individual differences in body-temperature regulation may be related to differences in individual reactions to noise, sleep loss, and other stresses. Experiments to evaluate this possibility are now in progress. In addition, they are evaluating both physiological and performance effects resulting from combinations of stresses which may work against each other, or in concert. For example, if heat produces an effect on performance, will this be aggravated or reduced by the presence of noise or sleep loss?

One early suggestion from the work of Dr. Teichner and his associates is that there is no such thing as an optimum environment; instead, there may be an optimally programmed environment for those engaged in complex performance for relatively long periods. ★

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HIGH-SPEED

MOTION-PICTURE PHOTOGRAPHY FOR USE IN DYNAMIC METALLOGRAPHY

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A modified Ellis-type high-speed framing camera has been developed under the direction of Professor M. L. Williams at the California Institute of Technology during the course of research sponsored by ARL under Contract No. AF 33(616)-6270. The intent was to develop a camera which could be used to study the flow and fracture behavior of metals through the taking of photomicrographs of metal surfaces using reflected light, including:

1. Velocity of slip band propagation
2. Kinetics and nature of crack propagation in large-grained polycrystalline specimens of pure metals
3. Kinetics and nature of cleavage in single crystals
4. Kinetics of ductile fracture in polycrystalline metals
5. Microcrack formation and propagation in metals under impact loading.

These capabilities were demonstrated by Professor Williams and his associates. Continued use is being made of this high-speed camera in research on crack propagation under the support of the Air Force Materials Laboratory, Research and Technology Division, AFSC.

The capabilities of the present camera with its associated light-source, high-speed Kerr Cell electronic shutter, and electronic controls include:

1. A variable framing rate from 10,000 to 100,000 frames per second
2. 128 total frames of 35-mm film in a continuous run
3. 400 foot of film capacity
4. Exposure time per frame adjustable between 0.05 to 0.4 microseconds

Illumination of the test sample is provided for by the use of a mercury arc light source which can run at steady state for alignment and focussing purposes. High-intensity pulses are applied to the lamp during photographic operations. The capabilities of the light source include:

1. A variable repetition rate from 10,000 to 100,000 pulses per second
2. A light intensity at the film plane of 3700 candle power during steady operation
3. A maximum light intensity at the film plane of 150,000 candle power during light pulses
4. Duration of light pulses is variable but normally set at 3 microseconds

The combined photographic capabilities of the camera and light source are:

1. Photomicrographic capability using reflected light:

   Reflective photomicrographs have been taken at 10X magnification using Kodak Tri-X film. The framing rate was 35,000 fps and the exposure was 0.1 μ second. Microscopic detail can be observed by making enlargements from the 35-mm film. Higher magnification can be obtained by making appropriate changes in the camera optics. The same type of photography can be carried out at framing rates up to 100,000 fps.

2. Photomacrographic capability using reflected light:

   Reflective photographs of a 1.0-inch-diameter region on the face of a specimen have been taken using Kodak Tri-X film. The framing rate was 35,000 fps and the exposure was 0.1 μ second. This type of photography can also be carried out at framing rates up to 100,000 fps.

3. Photomacrographic capability using transmitted light:

   Shadowgraphs of a 1.25-inch-diameter region of a specimen have been taken using Kodak Panatomic-X film. The framing rate was 100,000 fps and the exposure time was 0.1 μ second.

Details of camera design and operation can be found in the following references. ★

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NEW TRANSISTOR SHOWING GAIN INCREASE WITH CURRENT DECREASE

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A new transistor-amplification technique has been developed by scientists at AFCRL in which amplification (current gain) increases as current decreases. The new silicon transistor has been designated the Small Current-Amplifying Device (SCAD). A number of the devices have been fabricated for testing by AFCRL.

The transistor is essentially a field-effect (unipolar) transistor, but it combines certain advantages of both unipolar and bipolar transistors. It provides a relatively simple way of extending the range of transistors toward the very-low-current region. Current-amplification factors of 50 and greater have been obtained in experimental devices for signal levels between 1 microamp and .01 microamp at room temperature. At a temperature of 77 degrees K, a current amplification of 100 has been obtained for input signals of 1 microamp to .1 nanoamp. Conventional bipolar transistors cease to operate at this temperature and at these currents.

The new transistor operates on the principle of a forward-biased field-effect transistor, but is current-controlled in the manner of bipolar transistors. Essentially, this new device is a unipolar structure--that is, one in which majority carriers (holes in "p" material, electrons in "n" material) are controlled or modulated while flowing from the "source" contact to the "drain" contact. This modulation is effected by changes in the cross-sectional area of a narrow channel that connects the source and drain contacts. These changes in area occur in the depletion region. There is a contraction about the channel when the gate contacts are reverse-biased with respect to the source and drain. The unique AFCRL design employs a geometry that has the channel perpendicular to the semiconductor surface rather than parallel. This channel is completely pinched off by the depletion region at equilibrium--that is, when there is no bias. Thus, except when the transistor is performing its amplification function, it draws no current.

AFCRL is fabricating a number of these devices and is investigating such parameters as noise figure and frequency response. The silicon devices were made using advanced photolithographic, diffusion, and other techniques that make possible channel lengths of 8 microns, and channel widths of 2 microns (2×10^{-4} cm).

The new device offers several advantages over bipolar devices, with some of these advantages being shared with conventional unipolar transistors. These are: potentially greater resistance to radiation damage; lower temperature operation; and fabrication from less pure materials. ★

SPACE PHYSICS LABORATORY, AFCRL

Until recently it was generally assumed that the face of the moon we now see is essentially the same face presented several billion years ago. This assumption is now under question. Behind this re-evaluation is the simple fact that different regions of the moon have different numbers of craters for a given area.

The significance of this fact is only now being recognized. What the fact implies is this: if most of the moon's craters were made by meteorites, then the greater the number of craters per given area in a particular region, the older the region should be. Maria, or lunar seas (of the kind photographed by Ranger VII) have fewer craters than the rougher terrain surrounding them, indicating that they were probably formed somewhat later, perhaps by lava flowing onto the surface of the moon through cracks caused by the impacts of large meteors.

Attempts have been made to calculate the absolute ages of various features of the moon using this principle; but, because there is no reliable data on meteoroidal flux (the number of meteorites striking a given area of the moon's surface in a given time), estimates about the absolute age of lunar regions vary widely. However, AFCRL's Robert T. Dodd, Jr., John W. Salisbury, and Vern G. Smalley have used this principle to determine the sequence in which several lunar-surface features were formed, since this can be done without knowing the present or past flux of meteorites on a particular region.

In order to compensate somewhat for the gravitational focusing effect which the earth has on meteorites heading toward the moon, Dodd, Salisbury, and Smalley compared surfaces which were adjacent and therefore likely to be subject to the same flux of meteorites. They counted the craters in the three main maria north of the moon's equator--Mare Frigoris, Mare Imbrium, and Mare Serenitatis, and the craters of the Appeninian debris between Mare Imbrium and Mare Serenitatis. They found that these three maria are of similar, but not identical ages. Mare Frigoris is probably the oldest, and Mare Serenitatis the newest. The Appeninian debris is slightly older than any of the three maria. It contains many secondary craters, probably caused by the fall-back of large chunks of rock ejected by the great impact that formed Mare Imbrium.

The study of the sequence in which lunar features were formed is filled with a host of complicated factors, such as the obliteration of older craters by newer ones, and secondary craters caused by flying debris thrown out in the formation of primary craters. But possibly the greatest uncertainty complicating lunar studies concerns the very origin of most of the moon's craters. Scientific opinion divides evenly between the theory that they are meteoroidal and the theory that they are volcanic. This question may not be settled until men land on the moon, and perhaps not even then.

For the purposes of their study, Dodd, Salisbury, and Smalley assumed that most of the moon's craters were meteoroidal and that whatever volcanic craters existed were merely a possible source of error. However, they presently believe that the origin of most of the moon's craters may make no difference so far as their usefulness in determining the relative ages of lunar features is concerned. A new study is currently under way at AFCRL to see if this is so by examining the consequences of the assumption that most of the moon's craters are volcanic. ★

THE USE OF CONICAL NOZZLES IN A HYPERSONIC WIND TUNNEL

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The purpose of this note is to point out some advantages and disadvantages of conducting aerodynamic research in a hypersonic wind tunnel equipped with a conical nozzle as compared to one equipped with a contoured nozzle. It is most desirable to conduct all research in a contoured nozzle; however, no exact method is available for designing a contoured nozzle. Design techniques presently in use depend on source flow and contouring by the method of characteristic plus a correction for boundary-layer thickness. The boundary-layer-thickness correction is an empirical correction which is a function of both the Mach number and Reynolds number. This design technique yields a contoured nozzle which produces uniform parallel flow for one Mach number and Reynolds number only.

Some preliminary research carried out in the Aerospace Research Laboratories' 4-inch hypersonic wind tunnels at Mach numbers of 12 and 14 indicates that contoured nozzles have a very narrow range of operation with reference to Reynolds number and, when operating off-design, the longitudinal Mach-number gradient is reasonably good; however, the lateral Mach-number gradient presents some serious problems. For these reasons, and the fact that conical nozzles are easier and cheaper to construct as compared to a contoured nozzle, the conical nozzle is preferred by some investigators. Of course, the conical nozzle also presents certain problems. The advantage of a conical nozzle is that the range of Reynolds number over which the lateral Mach-number gradient is considered to be very good is appreciably greater than that of the contoured nozzle. The disadvantage is the fact that a longitudinal Mach-number gradient is present. Figures 1 and 2 are the results of tunnel-

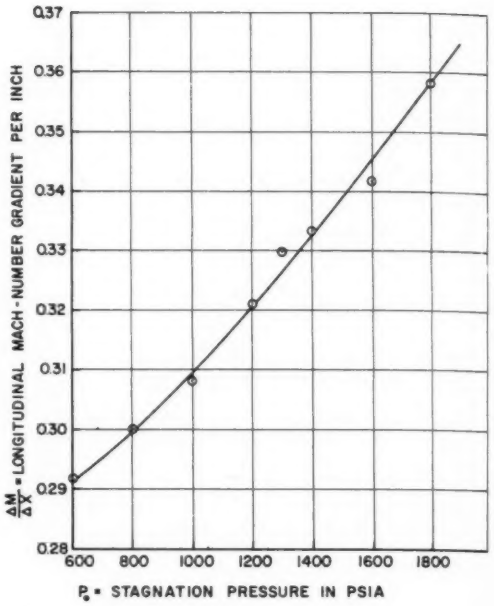

Fig. 1 Longitudinal Mach-Number Gradient versus Stagnation pressure in PSIA for T_o = 2200°R and for M_g = 14 (Conical)

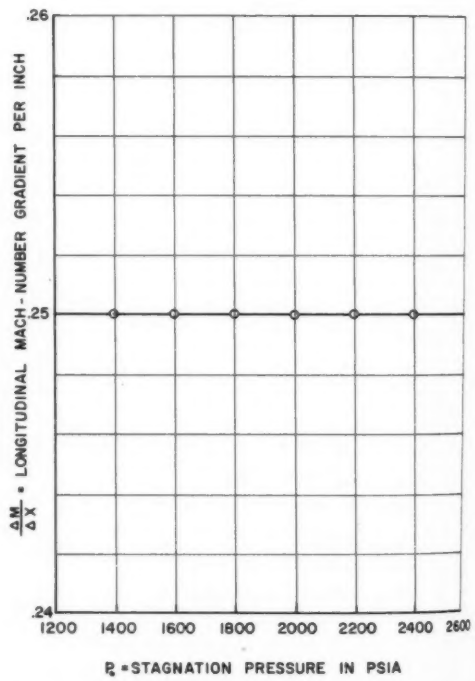

Fig. 2 Longitudinal Mach-Number Gradient per inch versus Stagnation Pressure in PSIA for T_o = 2200°R and M_g = 17 (Conical)

empty calibrations taken at a stagnation temperature of 2200° R for the 4-inch hypersonic wind-tunnel conical nozzles at geometric Mach numbers of 14 and 17, respectively. In Figure 1 it can be seen that, for the geometric Mach-number-14 nozzle, the longitudinal Mach-number gradient varies nonlinearly from $\Delta M/\Delta X = 0.2915$ per inch at a stagnation pressure of 600 psia to a value of $\Delta M/\Delta X = 0.358$ per inch at a stagnation pressure of 1800 psia. For a geometric Mach-number-17 nozzle, Figure 2 shows that the longitudinal Mach-number gradient is independent of the stagnation pressure and has a value of $\Delta M/\Delta X = 0.25$ per inch. This difference in the longitudinal Mach-number gradient between the two nozzles is not fully understood at this time.

Because of the presence of such large longitudinal Mach-number gradients in these conical nozzles, it becomes necessary to apply a correction to all the aerodynamic data in order to obtain the proper results. In an attempt to verify this point, a blunt flat plate at zero degrees angle of attack and flap deflection was tested in the 4-inch hypersonic wind tunnel with a Mach-number-14 conical nozzle. For purposes of comparison, the test conditions were taken similar to data obtained in reference 1 where a contoured nozzle was used. Both sets of data were taken at a nominal Mach number of 14.25 and at a Reynolds number per foot of 0.299×10^6. In both cases a thermal creep correction was applied. In the Aerospace Research Laboratories' facility, the longitudinal Mach-number-gradient correction used was taken from reference 2 and is of the form

$$P_{corr} = \frac{P_{tc}}{1 - \frac{43\gamma}{5(\gamma-1)(14+\gamma)}\left(\frac{X}{M}\right)\left(\frac{\Delta M}{\Delta X}\right)} \quad (1)$$

where

γ = ratio of specific heats for air.

X = location of specific orifice from the nose of the model in inches.

M = the free-stream Mach number.

$\frac{\Delta M}{\Delta X}$ = longitudinal Mach-number gradient per inch.

P_{tc} = the measured pressure in mm of Hg. abs. with thermal creep correction applied.

P_{corr} = the corrected pressure in mm of Hg. abs.

This data is presented in Figure 3 in a similarity parameter plot, namely, a plot of the ratio of local corrected pressure to the

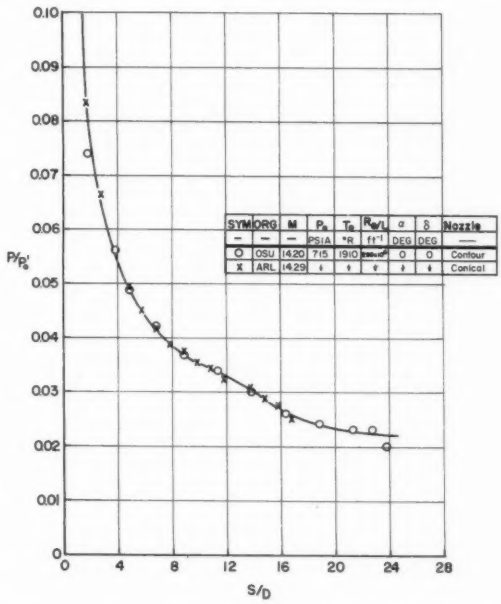

Fig. 3 P/P'_o versus S/D for a Blunt Flat Plate at $\alpha = \delta = 0°$

corrected stagnation-point pressure versus the dimensionless surface distance. As can be seen, the data obtained with a conical nozzle with the longitudinal Mach-number-gradient correction applied as given by Eq. (1) is in excellent agreement with similar data obtained in the Ohio State University facility with a contoured nozzle.

From this type of test one can conclude that conical nozzles are extremely useful for conducting basic aerodynamic research provided the proper longitudinal Mach-number-gradient corrections are applied. It must be

mentioned, however, that such corrections may be difficult to obtain mathematically since they are a function of such variables as model configuration, angle of attack, flap deflection, local shock waves, and local expansion fans. ★

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AFCRL MASS SPECTROMETER OBTAINS HIGH-PRECISION IONOSPHERIC DATA

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A mass spectrometer carried into the ionosphere aboard a rocket has given AFCRL scientists the clearest and most precise picture yet obtained of the ion structure of the ionosphere. The most surprising feature of the measurements was the high concentration of metallic ions in the nighttime E region. This concentration represented some 20 to 30 per cent of the total ion content of the ionosphere at about 95 km. The precision measurements also indicate that certain theoretical predictions on concentrations of N_2^+ and O_2^+ at altitudes below 75 km may be in error.

The AFCRL mass spectrometer was flown aboard a Nike Cajun rocket launched from Eglin AFB on 31 October 1963. It obtained an altitude of about 112 km. The spectrometer performed perfectly. Approximately 20 positive ion peaks were detected in the mass range 10 to 45 atomic-mass units at altitudes between 64 to 112 km. The predominant ions detected within the D region (64 to 82 km) were 18^+ (H_2O^+), 30^+ (NO^+), and 32^+ (O_2^+). In addition, there was an ion with an approximate mass of 37, which is probably a "cluster" ion, the primary mass of which is water vapor. At 83 km, the abundance of O_2^+ approaches that of NO^+, these being the predominant constituents above 83 km.

At 82.5 km, a sharp transition occurred in the ionosphere, characterized by the rapid disappearance of 18^+ and 37^+ and the instantaneous appearance of six new ion peaks. Five of these ion peaks are suggested to be the metallic ions of sodium (23^+), magnesium (24^+, 25^+, 26^+) and calcium (40^+). The metallic ions all exhibited identical altitude profiles, a 10-kilometer-wide concentration with maximum density at 95 km. This profile compares with the height distribution profile of meteor trails obtained by radio echo techniques. It is estimated that the magnesium ions comprise roughly 10 per cent of the total ion density at 95 km.

Mass spectrometers discriminate between atoms or molecules on the basis of their atomic mass. The AFCRL rocket-borne mass spectrometer is of the quadrupole type. The "quadrupole" refers to the fact that a key element consists of a core of four, three-inch stainless steel rods. The four rods are arranged in a square configuration; positive ions entering the system having a specific mass-to-charge ratio will traverse the length of the rods to a detector. All other ions entering the field are collected by the rods or by the surrounding envelope package before reaching the detector. Whether a specific ion reaches the detector or not depends on the rf and dc voltage of the rods. Thus, the mass spectrum is scanned by varying the rf and dc voltages, each scan requiring two seconds. Atomic masses from 1 to 46 can be measured.

The quadrupole mass-spectrometer system operates at a pressure in the 10^{-6} torr range. This vacuum is obtained by using a liquid-nitrogen chilled zeolite pump. Zeolite is a class of mineral with a unique ability to absorb molecules. To assure optimum performance of the vacuum pump using zeolite, several hours of processing and liquid-nitrogen chilling were required before launch of the mass spectrometer--with the liquid-nitrogen umbilical ejected only a few seconds before launch. ★

FLASHES OF INSIGHT

(FLASH PHOTOLYSIS AND FLASH SPECTROSCOPY)

DR. ALFRED WEISSLER
Directorate of Chemical Sciences, AFOSR

Insight into the ways in which materials are damaged by intense ultraviolet light is resulting from the research done by Dr. R. S. Berry at Yale University. His approach uses the combined method of flash photolysis and flash spectroscopy, as shown in Fig. 1. An intense flash of light is triggered by a Tesla discharge, and allowed to strike a thin film of solid material on the inside of an adjacent glass tube. The solid decomposes, evolving some gaseous products which are identified by their absorption spectra. The spectroscopic source is another, weaker light flash, which is set to go off at a precisely controlled time interval after the first, to provide an instantaneous photograph of the spectrum at that moment. By repeating the experiment with variation of the time delay between the two flashes, one can study the initial decomposition products and their changes during a very small fraction of a second.

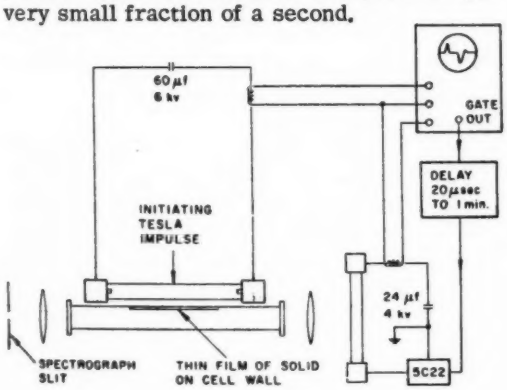
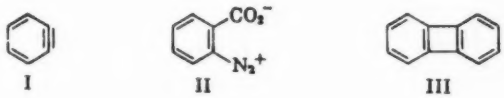


Fig. 1

Dr. Berry has applied this procedure in studying the formation and properties of the unstable substance, benzyne, C_6H_4. Benzyne is closely related to the important substance, benzene, C_6H_6, except that one of the double bonds in the conventional hexagon structure for benzene is replaced in benzyne by a triple bond (Fig. 2.I). When a thin film of benzenediazonium-2-carboxylate (II) was photolyzed, the spectrum obtained 60 microseconds after the photolytic flash showed a strong characteristic absorption which changed in a few minutes into that of biphenylene (III) formed by a joining up of two of the unstable benzyne molecules. Strong evidence was obtained that the initial absorption spectrum is due to benzyne, especially since similar results were obtained by photolyzing either orthoiodophenyl mercuric iodide or diorthophenyl mercury. By gas chromatography, both biphenylene and triphenylene were isolated from the products.



I II III

Fig. 2

The double-flash technique thus provides insights into the fundamental mechanisms through which intense light causes changes in the structure of molecules. ★

structure of the UPPER IONOSPHERE

UPPER ATMOSPHERE PHYSICS
LABORATORY, AFCRL

The uppermost layer of the ionosphere, the F_2 layer centered at roughly 300 km, is not an evenly featured mantle about the earth--a fact known for some time. The density of the free electrons and positive ions making up this layer varies widely with altitude and latitude. These variations have a definite pattern. Superimposed on this pattern, however, is a recently noted feature of consider-

able interest. In the south polar region, near the earth's magnetic equator, are found areas of marked irregularity. Within relatively short distances in these regions, the electron density fluctuates widely. These irregularities can be thought of as mottled, somewhat random patches of electrons.

These are some of the features of the F_2 layer uncovered in the past year or so by AFCRL scientists. The findings are derived from data from several AFCRL instrumented satellites. Electron-density measurements of the F_2 layer were made by standing wave impedance probes carried aboard these satellites. Because free electrons increase the impedance of an antenna in a linear fashion, the electron density of the medium can be measured fairly simply.

The picture of the F_2 layer which is now emerging was derived from data from several satellites covering a range of altitudes and having orbital configurations that permitted measurements at all latitudes. Results of these measurements will be published soon in an AFCRL report, "Direct Satellite Probe Measurements of Ionospheric Irregularities in the F Region and the Polar Cap," by J. C. Ulwick, W. Pfister, and R. E. McInerney of AFCRL.

The ionosphere is perhaps one of the most intensely studied of all natural phenomena. It is tenuous and fragile and easily disturbed. It changes with levels of solar activity; nuclear explosions can drastically alter its character; and even a missile passing through it can set off a train of perturbations. It exerts the single most important influence on radio energy. A vehicle passing through it has something of the effect of a rock thrown into a smooth lake. A disturbance is created, and this disturbance, properly characterized, could serve as an alarm.

One big advantage of the direct probing of the upper ionosphere by means of satellites is that precise measurements of electron concentrations at one particular altitude, latitude, and point in time can be made. But this very advantage is also a disadvantage. We can measure the same point in space but once, and then fleetingly. We cannot see the changes that take place at this particular point in space during the course of the day, from season to season, and at various levels of sunspot activity. But satellites permit us to sweep broadly over the earth's entire F_2 region, establishing data points from which interpolations can be made. The AFCRL investigators often found an amazing similarity in the F_2 electron-density profile between successive orbits even with a 22-degree longitudinal and a 90-minute time difference.

The various layers of increased electron densities (D, E, F layers), viewed in cross section, resemble somewhat the convoluted strata of old geological outcroppings. This general pattern is maintained through all the various ionospheric layers--from the D region out to the F_2 region. In the F_2 region and below, maximum and minimum densities of the layer at any given altitude occur at the same general latitudes. At the magnetic equator, we find minimum densities, with maximum densities occurring at about 20 degrees latitude. This pattern changes, however, at altitudes well above the F_2 layer. Here maximum densities occur at the magnetic equator, and decrease as we move toward the poles. Although we do find an increased electron density at high altitudes in the auroral regions, these densities may result from electrons in the outer radiation belt rather than in the ionosphere.

The AFCRL investigators have focused their immediate attention on the fine-structured irregularities superimposed on the general structure and occurring at well-defined positions at the magnetic equator and the south polar regions. Just why these small patches of electron density are found at these locations is a matter for further study. Two Blue Scout satellites are presently being instrumented by AFCRL to collect additional data on these irregularities. Besides these two planned satellites NASA, in late August, launched a special satellite to investigate the structure of the F_2 region. ★

A SEARCH for RAINY DAYS

concerning rainfall calendaricities

METEOROLOGY LABORATORY, AFCRL

Are there certain fixed calendar days (called "rainfall calendaricities" or singularities by meteorologists) every year on which rain is more likely to fall than it is on other days? The discovery that none exist probably won't shake anyone's faith in The Farmer's Almanac; but a study by AFCRL's Ralph Shapiro and Norman J. Macdonald, and the U.S. Weather Bureau's Glenn W. Brier, has shown that what some meteorologists thought were indications of the existence of such calendaricities were really misinterpretations of rainfall data.

This kind of discovery can easily be overlooked because of its negative character and because it fails to support some of the more intriguing, closely related ideas that meteorologists have put forward in the past few years. Yet, it is an important discovery because it may prevent unnecessary speculation about possible causes of rainfall calendaricities.

The idea that special rainfall dates recur yearly is probably as old as weather forecasting. Because observations also seemed to support the persistent belief in rainfall calendaricities, several theories have been advanced to account for them. A possible correlation between meteor showers and rainfall had been observed, and one theory held that, since the earth passes through certain swarms of meteorites at about the same time every year, the dust left by these meteorites, after they've burned up in the earth's atmosphere, filters down to provide nuclei for water vapor to condense around. It was later discovered, however, that meteorite dust doesn't behave that way. A much more satisfactory explanation of rainfall calendaricities was that the regular variation in the solar heating of a particular region of the earth, and the atmosphere above it, causes sharp changes in the flow characteristics of the atmosphere. The occurrence of these changes as regular as clockwork during the year could make it more likely to rain on the same days every year.

To give the rainfall-calendaricity hypothesis a much more thorough test than any it had previously been subjected to, Shapiro, Macdonald, and Brier programmed a computer to run a statistical analysis on U.S. precipitation data from January 1, 1900 through December 31, 1962. First, the seasonal variation was removed from the precipitation data, and the period of one exact year (365.2422 days) was divided into 100 equal classes. A decimal value was calculated for every date from January 1, 1900 to December 31, 1962, and each date was put into one of the 100 classes. Then the number of classes whose precipitation index showed more than a chance variation from the average of all the classes were counted, and it was found that there were as many classes that varied significantly from average as could be expected by chance. In addition, the same data was then used for 56 other periods, ranging from four days shorter than a year to four days longer than a year, each divided into 100 classes. If rainfall calendaricities existed, there should have been a greater number of classes which varied significantly from average rainfall in a period of a year than in periods of other lengths. However, this was not the case. Many of the other periods used (both longer and shorter than a year) had as many or more classes which varied significantly from the average rainfall, confirming the fact that there is nothing unique about 365.2422 days as far as occurrence of precipitation in the U.S. is concerned. ★

OAR profiles

Captain George F. Heinrich, author of the article, "Measurement of Drift Mobilities in Piezoelectric Semiconductors," which appears in this issue of the Review, is a scientist with the Solid State Physics Laboratory, ARL. He is a 1954 graduate of the U.S. Naval Academy, Annapolis, Md. He not only has a B.S. from the Academy, but also an M.S. in Nuclear Engineering from the Air Force Institute of Technology, Wright-Patterson AFB, Ohio, 1961-1963.

Mr. Rollin E. Hook, a scientist with the Metallurgy and Ceramics Research Laboratory, ARL, writes in this Review on "High-Speed Motion-Picture Photography for Use in Dynamic Metallography." He has a B.Sc. in Metallurgical Engineering from Purdue University, West Lafayette, Indiana (1962) and an M.S. in Metallurgical Engineering from O.S.U., Wright-Patterson AFB, Ohio (1959). From 1956 to 1957, he was employed as a metallurgist with the Dow Chemical Company Research Laboratory, and from 1957 to 1960 served as a 1st Lt in the USAF. He is a member of several professional societies, and received the Outstanding Achievement Award for 1962, Dayton Area National Engineers Week.

Dr. David Atlas, author of "Angels in Focus" which appears in this issue of the Review, is shown receiving the Marcus O'Day Award from Brig Gen B. G. Holzman, Commander of AFCRL. This award is presented each year to the AFCRL scientist who publishes the most outstanding research paper in a reputable scientific journal.

Dr. Atlas is Chief, Weather Radar Branch, Meteorology Laboratory, AFCRL. He has a B.S. degree from New York University (1946), and an M.Sc. degree (1951) and D.Sc. degree (1955), both from M.I.T. After meteorology and radar training in World War II, Dr. Atlas served as a radar weather officer with the All Weather Flying Division, Air Materiel Command. After discharge in October 1946, he stayed on as a civilian radar meteorologist, conducting research and development on the objective use of weather radar, especially for storm avoidance. He is responsible for the invention of "iso-echo" radar storm contour mapping which is in wide use in airborne weather radars and ground radars as well.

Dr. Atlas joined AFCRL in 1948, and has been in charge of weather radar research since then. In addition to pursuing the quantitative uses of radar as an atmospheric research and observing tool, he has made the following significant contributions: (1) the first radar detection and probing of the sea breeze; (2) radar detection of lightning discharges from the tops of thunderstorms; (3) initial findings of phenomenal radar cross sections of large, dry hailstones and the effects of melting; (4) conception of multiwave-length radar techniques for the measurement of hailstone sizes. He has also published extensively on the characteristics of radar "angel" echoes.

Dr. Atlas has a number of publications and awards to his credit.

ANGELS in FOCUS
(phantom blips on radar screens)

METEOROLOGY LABORATORY, AFCRL

Phantom blips known as "dot angels" have appeared on radar screens since the beginning of radar. They are seen at rather unpredictable intervals and often on clear, cloudless days. Explanations for the angels have ranged from flying saucers to birds and insects. AFCRL's David Atlas has compiled a set of dot-angel characteristics from a number of independent radar observations and has presented a detailed model to account for the dot angel.

Most dot angels have been detected by vertically pointing radars. The fact that an angel focuses more of the beam back toward the antenna as it approaches the zenith provides an essential clue. A curved reflector, presenting a concave surface to a radar beam, would produce this effect, particularly if its curvature were spherical.

How are these curved reflectors formed? First, two inhomogeneous air layers are needed, the inhomogeniety resulting from temperature differences. The two layers thus have different indexes of refraction. If we then have a convective thermal in the lower layer of air--that is, a vertical column of rising air--the air column will push up into the upper layer. This forms a bubble along the line separating the two layers. The bubble is hemispherical and, if Atlas' theory is correct, as observations indicate it is, then the 'cap' or topmost part of the bubble reflects the radar signal almost perfectly. For the bubble to reflect perfectly, however, the sharp gradient of refractive index at the top of the cap must be smooth to a fraction of a wave length. The need for such a well-shaped surface is implied by the maximum occurrence of dot angels on calm days and their disappearance where the surface winds exceed 20 to 25 knots.

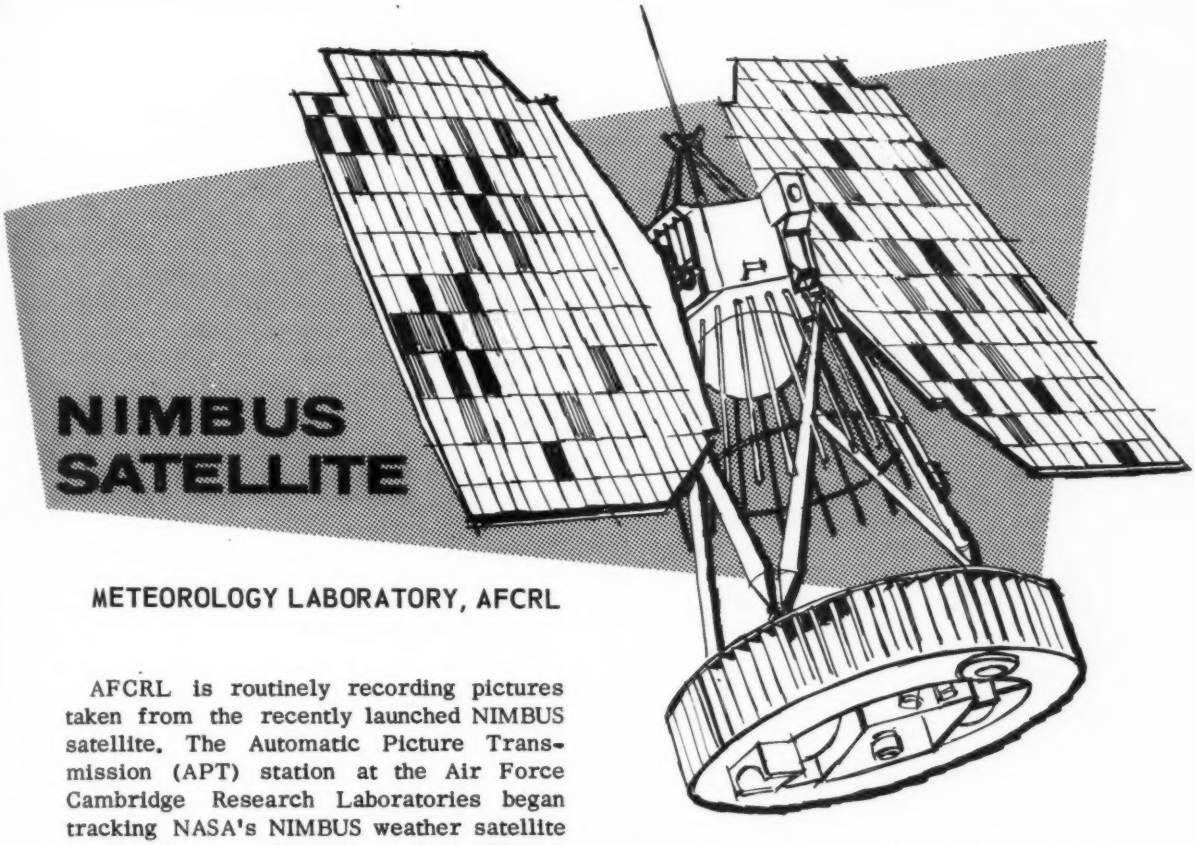
This model also accounts for another dot-angel characteristic, namely, its appearance as a point source. The angel is seen as a point source because only one point on a spherical reflector, the point at which a plane tangent to the surface of the reflector is perpendicular to the incident beam, will reflect the beam back along the same path.

Their shape also explains a curious inconsistency in past radar observations. With a Doppler radar pointing vertically, the angels always appear to move upward--which in fact they do. But with a non-Doppler tracking radar, looking at an angle, the angel seems to move either up or down depending on whether the angel is moving toward the radar or away. When we look at the simple geometry of the matter, we see that, as the natural reflector moves toward the radar beam, the point on the curved surface from which the signal is reflected moves upward. As the angel moves away, the point source moves downward. The result is a false indication of upward and downward velocity.

It was also found that the amount of power reflected back from an angel increases as the angel gains altitude, and that this increase is proportional to the square of the distance from the radar to the angel. This fact suggests that the radius of curvature of the atmospheric reflector is directly proportional to altitude. Its area, and thus the amount of power it reflects, is proportional to the square of the altitude. ★

SCIENTIFIC NOTE

Rocket Launches Planned from Aircraft Carrier: AFCRL will launch six rockets next January off the coast of Peru from a converted aircraft carrier. The AFCRL flights will coincide with other shipboard launchings by NASA which operates the unique mobile platform. Four of the AFCRL rockets will be magnetometer-equipped Nike Apache sounding rockets. The other two will be Nike Cajuns to investigate positive ion and electron densities, energies and temperatures. All six firings are designed to gather data on the equatorial electrojet. The electrojet is a 660-km-wide band of eastward current of charged particles in the ionosphere centered over the magnetic equator in the E region at about 100 km. As a result of these measurements, more will be learned about the intensity, altitude and thickness of the electrojet. (Upper Atmosphere Physics Laboratory, AFCRL)



METEOROLOGY LABORATORY, AFCRL

AFCRL is routinely recording pictures taken from the recently launched NIMBUS satellite. The Automatic Picture Transmission (APT) station at the Air Force Cambridge Research Laboratories began tracking NASA's NIMBUS weather satellite on Friday, the 28th of August 1964. It acquired the first of a series of high-resolution pictures of hemispheric cloud cover at 1:20 that afternoon. NIMBUS was launched that morning from the Pacific Missile Range.

The experimental station at AFCRL is one of six key stations which are providing NASA with information about the performance of NIMBUS in its initial picture-taking passes, advising the space agency as to the performance of the electronic receiving equipment, and evaluating the meteorological usefulness of the pictures taken.

The Satellite Meteorology Branch headed by Mr. Thomas Keegan operates this APT station in AFCRL's Meteorology Laboratory. This group also tracked the TIROS VIII weather satellite when it was launched in December 1963.

It takes about three and one half minutes for ground stations to record cloud pictures taken by NIMBUS' earth-pointing camera. Two recording methods are used. One, a facsimile system, the other photographic. The Polaroid photographic system which converts the electronic signal from the satellite into a light beam projected onto sensitized film, provides the clearer picture.

The AFCRL station tracks NIMBUS for an average of three passes each day. NIMBUS is now in an elliptical earth orbit with an apogee of 501 miles and a perigee of 227 miles. The satellite crosses the equator over the Boston area near local noon time, daily.

The APT station at AFCRL provides NIMBUS cloud pictures from as far south as the north coast of South America up to Hudson Bay on the north, to Texas and Utah on the west and the mid-Atlantic Ocean on the east.

Of the estimated 50 world-wide APT stations, 20 of them are Air Force units. ★

measurement of drift mobilities in piezoelectric SEMICONDUCTORS

CAPTAIN GEORGE F. HEINRICH
Solid State Physics Laboratory, ARL

Past studies of the transport properties of the majority charge carriers in semiconducting crystals have primarily consisted of Hall mobility studies. The Hall mobility has then been related to the conductivity mobility through a correction factor which depends on the type of scattering of the charge carriers and the degeneracy. A limitation of these studies is that the conductivity mobility is not always a complete indication of the charge-carrier transport properties since the conductivity mobility does not give any indication of the trapping of the charge carriers.

The drift mobility, which is defined as the drift velocity of the injected carriers divided by the electric field, takes into account trapping and is generally smaller than the conductivity mobility.

There have been several methods used to measure the drift mobility in semiconductor crystals, but all methods have limitations. Probably the best known is the Haynes-Shockley method.[1] The Haynes-Shockley technique involves injecting a pulse of minority carriers into the crystal and measuring the time of transit over a known distance when a dc-field is applied to the crystal. The major drawback to the Haynes-Shockley method is that only the drift mobility of the minority carriers can be measured. Another well-known method of obtaining drift mobilities is by the measurement of the photoconductivity gain and decay time.[2] However, this method is handicapped by the difficulty of obtaining a true lifetime of the charge carriers in a crystal that has several different trapping levels.

In 1961, scientists of the Bell Laboratories[3] showed theoretically and experimentally that high-frequency stress waves could be attenuated or amplified in CdS by an energy exchange between conduction electrons and the stress wave. The energy exchange takes place because the conduction electrons are "coupled" to the stress wave through the piezoelectric field traveling with the stress wave. If a high electric field is applied to the crystal and the electrons are forced to drift faster than the stress wave, the stress wave is amplified. If the electrons are drifting slower than the stress wave, the stress wave is attenuated. When the electrons and stress wave are traveling at exactly the same velocity, the stress is neither attenuated nor amplified. By measuring the dc-drift voltage applied to the crystal at the point of no energy exchange, the drift mobility is determined from $\mu = {}^{v_d}/_{E}$ where v_d is the magnitude of the velocity of the stress wave and E is the magnitude of the applied electric field. Due to a phase shift between the trapped carriers and the stress wave, a small correction should be applied to the drift mobility.[4] The stress-wave method of obtaining electron-drift mobilities is limited to piezoelectric semiconductors in the resistivity range of 10^3 to 10^5 ohm -cm.

In recent studies at ARL, the drift and Hall mobilities of doped and undoped CdS, CdSe and CdS:Se single crystals have been measured. Results at room temperature on two undoped CdS crystals are shown in Figure 1.

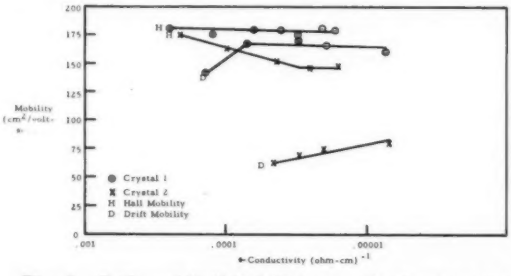


Fig. 1 Drift and Hall Mobilities vs Conductivity for Undoped Crystals

The Hall mobilities of the CdS crystals agree fairly well with similar previous CdS Hall mobility measurements made in the resistivity range[5] 10^3 to 10^5 ohm -cm. The Hall and drift mobilities of crystal 1 are nearly the same. However, for crystal 2 the Hall and drift mobilities are appreciably different. Mass spectrographic analysis of the crystals revealed appreciably greater amount of im-

purities in crystal 2 than in crystal 1.

Investigations of the Hall and drift mobilities are continuing in conjunction with the crystal-growing program at ARL. Different methods of heat treatment are now being investigated in order to determine what effect these treatments have on the transport properties of CdS, CdSe and CdS:Se. Also, crystals are being doped with the alkali metals in order to determine what effect these dopants have upon the transport properties. ★

1. *Shockley, William, Electrons and Holes in Semiconductors, New York: D. Van Nostrand Co., Inc., 1950.*
2. *Bube, R. H., Photoconductivity of Solids, New York: John Wiley and Sons, Inc., 1960.*
3. *Hutson, A. R., J. H. McFee and D. L. White, "Ultrasonic Amplification in CdS," Physical Review Letters, 7, 237-9, Sep 15, 1961.*
4. *Ishiguro, T., I. Uchida and T. Suzuki, "Effect of Trapping of Free Carriers in CdS Ultrasonic Amplifier," Journal of the Physical Society of Japan, 19, 674-680, May 1964.*
5. *Bube, R. H. and H. E. MacDonald, "Effect of Photoexcitation on the Mobility in Photoconducting Insulators," Physical Review, 121, 473-483, Jan 15, 1961.*

SINGLET-SINGLET ENERGY TRANSFER IN FLUID SOLUTIONS

DR. JEAN T. DUBOIS

Chemistry Research Laboratory, ARL

The transfer of electronic excitation energy between complex molecules has been the subject of a continuing program of research at ARL. This is a process whereby electronic energy initially acquired by a species A is passed on to a species B. Its usefulness resides in the fact that when A and B are exposed to a common source of energy, B may be completely transparent to the energy source and yet acquire energy by borrowing it from A which itself is nontransparent. Knowing the rules governing such transfers makes it possible to study the reactivities of certain excited states of B which are not normally accessible by direct absorption of energy, and makes it possible to promote reactions of B or to quench reactions of A by channelling the energy of A into B.

In previous reports on this research[1,2], it was shown that when species B was biacetyl and the excited species of A was a singlet state, the transfer reaction appeared to be controlled by the rate of diffusion of energized A toward B; a detailed reaction mechanism explaining these facts was also established. That these reactions should be controlled by diffusion, however, was somewhat of a puzzle. The previously accepted theory of interaction between a singlet excited state of A and a singlet and excited state of B usually predicts such interactions to be long-range, i.e., not requiring actual physical contact between the transferring species, and therefore not accountable by diffusion-controlled encounters. Further examples of energy transfer from excited singlet A molecules to biacetyl were then studied experimentally to test the generality of the previous observations and to reconcile the observed diffusion-controlled nature of the transfer process with the existing body of theory. The following excited A molecules were used as donors of energy to biacetyl: diethyl ketone, methyl ethyl ketone, cyclopentanone, phenanthrene and chrysene. In each case the transfer reaction was monitored in two ways: 1) by observing the quenching of the fluorescence of A by biacetyl; and 2) by observing the sensitization of the fluorescence of biacetyl by A molecules. The over-all results obey the postulated diffusive mechanism, thus establishing its generality; a theoretical calculation of the interaction of the excited singlets of A with biacetyl clearly rules out long-range interactions for these systems. The latter result is now easily understood in terms of the very-low molar extinction coefficient of the acceptor biacetyl.

The objectives of this investigation were met successfully, and it may be said that the new knowledge now available brings us one step closer to the rational application of the techniques of the quenching and sensitization of luminescence. Details of this work have been published in the Journal of Chemical Physics. ★

1. *Dubois, Jean T., OAR Research Review, April 1962.*
2. *Dubois, J. T. and B. Stevens, Luminescence of Organic and Inorganic Materials, John Wiley and Sons, Inc., 1962, p. 115; also ARL 62-402.*

NIMBUS
weather satellite hits jackpot

Photo 1 *This helix antenna located on the roof of AFCRL's main laboratory building was used to pick up the first photographs relayed from the NIMBUS weather satellite soon after its launch on Friday, 28 August 1964. The AFCRL Satellite Meteorology Branch has collected hundreds of photographs transmitted from the NIMBUS Satellite, photographs of remarkable quality. The antenna is part of the APT (Automatic Picture Transmission) system developed especially for use with the NIMBUS satellite. It is one of twenty stations operated by the Air Force.*

Photo 2 *This is the equipment used at AFCRL for recording the pictures taken from the NIMBUS weather satellite. The girl in the photograph is Arlene Cincotta of the Meteorology Laboratory.*

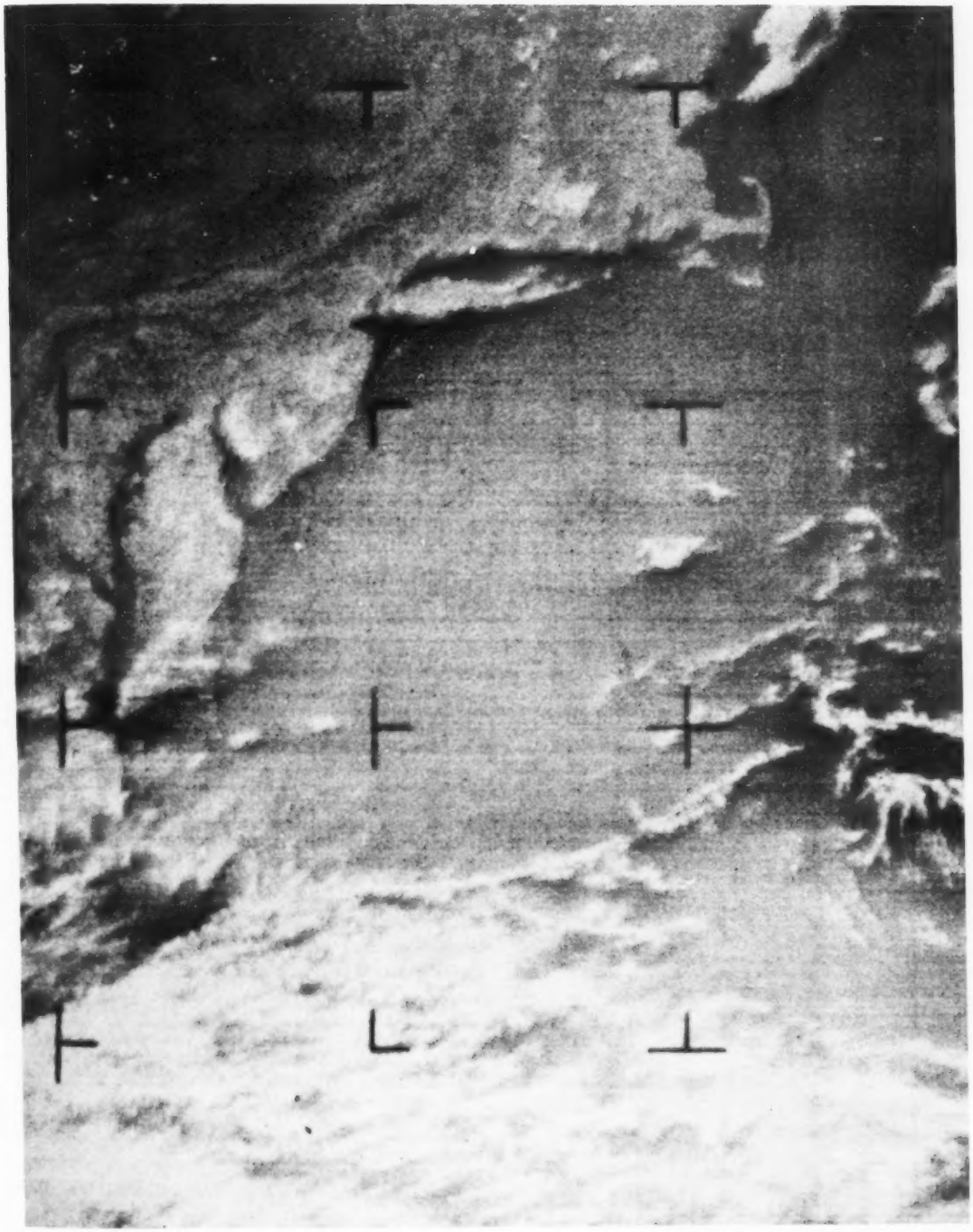


Photo 3 *This is one of the photographs relayed recently from the NIMBUS weather satellite. It shows one of the clearest views recorded of the East coast of the United States. The cloud layer at the bottom of the photograph is an advanced layer of Hurricane Dora.*

SCIENCE FAIR WINNERS SHINE AT *AFCRL*

Seated before the laboratory apparatus is Eric O. Wright of *Lawrence, Kansas, a National Science Fair winner who was assigned to AFCRL's Biophysics Branch, Data Sciences Laboratory, during his stay this past summer. His work at AFCRL was concerned with experiments dealing with electrical activities in the brains of rats. He was visited by his family on his last day at AFCRL. From left to right they are his mother, Mrs. M. E. Wright, his brother, Woody, Eric (discussing the laboratory apparatus with his family), his father, Dr. M. E. Wright, and his sister, Colleen. (David A. Matthews, another Science Fair winner, can be seen in the upper left-hand corner of the photo.)*

David A. Matthews of Washington, D.C., one of the National Science Fair winners who worked at AFCRL this past summer, is shown aboard a C-130 aircraft used by AFCRL in meteorological research. During his stay at AFCRL, David worked in the area of sattellite meteorology. He received his Science Fair Award on the basis of his study on "Extratropical Cyclones."

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